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**WO 03/087016 A1**

(54) Title: METHOD OF MAKING A HEATING ELEMENT OF MOLYBDENUM SILICIDE TYPE

(57) Abstract: The present invention relates to a method of producing a heating element that is comprised essentially of molybdenum silicide and alloys of this basic material, which forms aluminium oxide on its surface. The invention is characterised by producing a material that contains substantially  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$  by mixing a mixture of a silicon and molybdenum compound with an aluminium compound; in that the silicon and molybdenum compound either include  $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$  and are mixed either with an aluminium compound consisting of  $\text{Al}_2\text{O}_3$  or  $\text{Al}(\text{OH})_3$  and possibly mixed with one or more of the compounds  $\text{SiO}_2$ ,  $\text{Si}$  and  $\text{MoO}_3$  or by virtue of the mixture of the silicon and molybdenum compound containing  $\text{MoO}_3$  and  $\text{Al}$  and  $\text{Si}$  and/or  $\text{SiO}_2$ ; in that the input components together have a degree of purity corresponding to at least 98%; and in that the mixture is caused to react exothermically and/or by being sintered so that exchange reactions are caused to take place, to form the compounds  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$ , where  $x$  is caused to lie in the range of 0.4 - 0.6.

Method of making a heating element of molybdenum silicide type.

The present invention relates to a method of manufacturing a  
5 heating element of the molybdenum silicide type.

An electric resistance element of the molybdenum silicide type is described in Swedish Patent Specifications 0003512-1 and 0004329-9. According to patent specification 0003512-1  
10 the resistance material of the heating element includes  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  which is caused to contain aluminium to an extent at which the formation of pest is essentially prevented.

It has been found that when such material is operated in a  
15 temperature range of 400 - 600°C no pest, or only a slight amount of pest, is formed. Pest is formed by virtue of the formation of  $\text{MoO}_3$  from  $\text{MoSi}_2$  and  $\text{O}_2$ .

The reason why the formation of pest is significantly reduced  
20 or is eliminated is due the formation of  $\text{Al}_2\text{O}_3$ , or a layer rich in  $\text{Al}_2\text{O}_3$ , on the surface of the element

The other patent specification 0004329-9 teaches a method of increasing the useful life span of heating elements that  
25 essentially consist of molybdenum silicide and alloys of this basic material when the element operates at high temperatures.

According to this patent specification, the heating element  
30 is caused to contain aluminium to an extent which is sufficient to maintain a stable, slowly growing layer of aluminium oxide on the surface of the heating element.

According to one preferred embodiment the heating element material is caused to contain  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ , where  $x$  lies in the range of 0.2 - 0.6.

- 5 A material of the molybdenum silicide type that contains aluminium has been found to possess improved corrosion properties at both low and high temperatures.

Such material is often produced by mixing  $\text{MoSi}_2$  powder with  
10 oxidic raw material, such as aluminosilicates. When the raw material is bentonite clay, there is obtained a relatively low melting point which contributes towards so-called smelt phase sintering which results in dense materials that contains  $\text{MoSi}_2$  and a proportion of aluminium silicate corresponding to 15 - 20 percent by volume.  
15

Bentonite clay containing chiefly  $\text{SiO}_2$  can be used in the production of heating elements containing  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ . When sintering with an Al-alloyed silicide there takes place a  
20 chemical exchange reaction in which the greater affinity of the oxygen to Al than to Si results in Si leaving the aluminium silicate and entering the silicide as a result of Al leaving the silicide and being sucked up by the oxide phase. This exchange reaction also contributes towards improved  
25 sintering properties of the composite material. The final material contains  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  that is substantially deplete of Al, where the oxide phase contains  $\text{Al}_2\text{O}_3$  in all essentials.

The standard procedure of manufacture involves mixing molybdenum, silicon and aluminium in powder form and firing the powder mix normally under a shielding gas atmosphere. This results in a cake of the material  $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$ , where  $y$  is larger than  $x$  in the above formula as a result of said ex-

change reaction. The reaction is exothermic. The cake is then crushed and ground down to a fine particle size normally in the order of 1 - 20 $\mu\text{m}$ . This powder is mixed with bentonite clay such as to form a wet ceramic material. The material is extruded and dried to a rod form whose diameter corresponds to the diameter of the subsequent heating element. The material is then sintered at a temperature that exceeds the smelting temperature of the bentonite component.

10 However, there is a drawback with an element of this kind. The problem is that the oxide that forms on the surface of the element, namely  $\text{Al}_2\text{O}_3$ ; sometimes, peels away or flakes off, i.e. loosens from the surface of the element in cyclic operation.

15 A peeling oxide gives poorer protection against continued oxidation of aluminium which becomes impoverished in the outer surface of the element more quickly. Moreover, oxide peelings can contaminate the oven in which the element is fitted, with the risk that performance and the appearance of products heat treated in ovens that have such elements will be significantly impaired. This thus restricts the use of such elements in heating processes.

20 25 This problem is solved by the solution taught in each of the two Swedish Patent Specifications 0201042-9 and 0201043-7.

Swedish Patent Specification 0201042-9 teaches a method of producing a heating element that comprises substantially of molybdenum silicide and alloys of this basic material. The method is characterised by producing a material that contains chiefly  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$  by mixing molybdenum alum-

nosilicide ( $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$ ) with  $\text{SiO}_2$ , where the  $\text{SiO}_2$  is at least 98% pure.

Swedish Patent Specification 0201043-7 teaches the production 5 of a corresponding material, where bentonite clay is used to add silicon dioxide and aluminium oxide. The bentonite clay shall have a contaminating substance content of less than 2000ppm.

10 It has been found surprisingly that there is obtained at low contaminant consistencies an oxide which does not peel after cyclic operation between room temperature and high temperatures, for instance 1500°C. The present invention is based on the insight that such a pure aluminium-oxide building molybdenum silicide material can be produced beneficially by beginning partly with other material and compounds than those 15 given above.

The present method of production of a heating element that is 20 comprised essentially of molybdenum silicide and its alloys includes the step of producing a material that contains essentially  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$  by mixing a mixture of silicon and molybdenum compound with an aluminium compound.

25 According to the invention silicon and the molybdenum compound include  $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$  and are mixed with either an aluminium compound consisting of  $\text{Al}_2\text{O}_3$  or  $\text{Al}(\text{OH})_3$ , and are optionally mixed with one or more of the compounds  $\text{SiO}_2$ , Si and  $\text{MoO}_3$ .

30 According to a second embodiment, silicon and the molybdenum compound contain  $\text{MoO}_3$  and Al and Si and/or  $\text{SiO}_2$ .

According to the invention the input components together have a degree of purity of at least 98%.

According to a preferred embodiment of the invention the 5 input components have a degree of purity of at least 99%.

The mixture is caused to react exothermically and/or by being sintered so that exchange reactions take place, to form the compounds  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$ , where x is caused to lie in 10 the range of 0.4 - 0.6.

There is obtained by this method an element material that is aluminium oxide building and whose aluminium oxide layers will not peel or flake; which was mentioned as a problem in 15 the beginning of this document.

According to one preferred embodiment x is caused to lie in the range of 0.45 - 0.55.

20 According to one preferred embodiment the  $\text{SiO}_2$  is included in silicates, where remaining substances in the silicate have properties that molybdenum silicide is unable to alloy with said substance or substances and have such properties that the symmetry of the crystal lattice of the molybdenum silicide is retained.  
25

It is possible to substitute molybdenum partly with Re, W or Nb in the material  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  without changing the symmetry of the crystal lattice.

30 Molybdenum can be replaced with tungsten (W) by an amount corresponding approximately to one third.

According to one preferred embodiment one or more of the following sintering auxiliaries MgO, CaO, SiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> is/are caused to be added to the mixture.

- 5 The present invention thus solves the problem mentioned in the introduction and enables the present element to be used beneficially in ovens without detriment to the material treated in the oven.
- 10 The present invention shall not be considered to be limited to the aforedescribed embodiments, since variations can be made within the scope of the accompanying claims.

## CLAIMS

1. A method of producing a heating element that is comprised essentially of molybdenum silicide and alloys of this basic material, which forms aluminium oxide on its surface, characterised by producing a material that contains substantially  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$  by mixing a mixture of a silicon and molybdenum compound with an aluminium compound; in that the silicon and molybdenum compound either include  $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$  and are mixed with either an aluminium compound consisting of  $\text{Al}_2\text{O}_3$  or  $\text{Al}(\text{OH})_3$  and possibly mixed with one or more of the compounds  $\text{SiO}_2$ ,  $\text{Si}$  and  $\text{MoO}_3$  or by virtue of the mixture of the silicon and molybdenum compound containing  $\text{MoO}_3$  and  $\text{Al}$  and  $\text{Si}$  and/or  $\text{SiO}_2$ ; in that the input components together have a degree of purity corresponding to at least 98%; and in that the mixture is caused to react exothermically and/or by being sintered so that exchange reactions are caused to take place, to form the compounds  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$  and  $\text{Al}_2\text{O}_3$ , where  $x$  is caused to lie in the range of 0.4 - 0.6.

2. A method according to Claim 1, characterised in that said  $\text{SiO}_2$  is included in silicates, where remaining substances in the silicate have properties such that molybdenum silicide is unable to alloy with said substance or substances and have such properties that the symmetry of the crystal lattice of the molybdenum silicide is retained.

3. A method according to Claim 1 or 2, characterised in that  $x$  is caused to lie in the range of 0.45 - 0.55.

4. A method according to Claim 1 2 or 3, characterised by adding one or more of the following sintering auxiliaries  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Y}_2\text{O}_3$  to said mixture.

5. A method according to Claim 1 2, 3 or 4, characterised by substituting molybdenum partly with Re or W or Nb in the material  $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ .

5

6. A method according to Claim 5, characterised by replacing molybdenum with W in an amount corresponding to approximately one third.

10 7. A method according to any one of the preceding Claims, characterised in that the input components have a degree of purity of at least 99%.

## INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

**IPC7: C04B 35/58, C22C 29/18, H05B 3/14**  
 According to International Patent Classification (IPC) or to both national classification and IPC

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**SE, DK, FI, NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**WPI DATA, EPO-INTERNAL**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 179100 A (METALLWERK PLANSEE GESELLSCHAFT M.B.H. IN REUTTE (TIROL)), 10 July 1954 (10.07.54) --	1-7
A	US 3269806 A (ERICH FITZER ET AL), 30 August 1966 (30.08.66) --	1-7
A	GB 899464 A (AKTIEBOLAGET KANTHAL), 20 June 1962 (20.06.62) -- -----	1-7

Further documents are listed in the continuation of Box C.  See patent family annex.

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